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(54) Title: PREPARATION OF ZEOLITES USING ORGANIC TEMPLATE AND AMINE

(57) Abstract

Crystalline zeolites are prepared using a small quantity of an organic templating compound and a larger quantity of an amine component containing at least one amine having from one to eight carbon atoms, ammonium hydroxide, or mixtures thereof.

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- 1 -

01 PREPARATION OF ZEOLITES USING
02 ORGANIC TEMPLATE AND AMINE
03

04 BACKGROUND OF THE INVENTION
05

06 Natural and synthetic zeolitic crystalline aluminosilicates
07 are useful as catalysts and adsorbents. These
08 aluminosilicates have distinct crystal structures which are
09 demonstrated by X-ray diffraction. The crystal structure
10 defines cavities and pores which are characteristic of the
11 different species. The adsorptive and catalytic properties
12 of each crystalline aluminosilicate are determined in part
13 by the dimensions of its pores and cavities. Thus, the
14 utility of a particular zeolite in a particular application
15 depends at least partly on its crystal structure.
16

17 Because of their unique molecular sieving characteristics,
18 as well as their catalytic properties, crystalline
19 aluminosilicates are especially useful in such applications
20 as gas drying and separation and hydrocarbon conversion.
21 Although many different crystalline aluminosilicates and
22 silicates have been disclosed, there is a continuing need
23 for new zeolites and silicates with desirable properties for
24 gas separation and drying, hydrocarbon and chemical
25 conversions, and other applications.
26

27 Crystalline aluminosilicates are usually prepared from
28 aqueous reaction mixtures containing alkali or alkaline
29 earth metal oxides, silica, and alumina. "Nitrogenous
30 zeolites" have been prepared from reaction mixtures
31 containing an organic templating agent, usually a
32 nitrogen-containing organic cation. Use of adamantane
33 materials as the templates for making molecular sieves,
34 particularly zeolites, is disclosed in U.S. Patent

-2-

01 No. 4,665,110, issued May 12, 1987 to Zones which is hereby
02 incorporated by reference. Adamantane materials are used as
03 the templates in making a particular zeolite, SSZ-25, as
04 disclosed in U.S. Patent No. 4,826,667, issued May 2, 1989
05 to Zones et al., and co-pending application No. 788,656
06 filed November 6, 1991, which is a continuation of U.S.
07 Serial No. 333,666 filed April 5, 1989, both of which are
08 hereby incorporated by reference. Use of hexamethyleneimine
09 as the sole template in making zeolites similar to SSZ-25 is
10 disclosed in U.S. Patents No. 4,439,409, issued March 27,
11 1984 to Puppe et al., and 4,954,325, issued September 4,
12 1990 to Rubin et al., while use of hexamethyleneimine and
13 piperidine as the template in making a zeolite similar to
14 SSZ-25 is disclosed in European Patent Application
15 No. 0,293,032 A2, dated May 11, 1988. Use of adamantanamine
16 materials in making a zeolite other than SSZ-25 is disclosed
17 in U.K. Pat. Application GB 2,193,202 A, dated February 3,
18 1988. Another zeolite utilizing amines in its manufacture
19 is the intermediate pore-size zeolite ZSM-5. U.S. Patent
20 No. 4,495,166, issued January 22, 1985 to Calvert et al.,
21 discloses use of a small amount of a quaternary ammonium
22 compound such as tetrapropyl ammonium in conjunction with
23 other amines to make ZSM-5.

24

25 U.S. Patent No. 5,057,296, issued October 15, 1991 to Beck,
26 discloses a process for producing ultra-large pore
27 (sometimes called "mesoporous") crystalline materials using
28 a two component system containing an organic template and an
29 amine. These mesoporous materials have uniformly sized
30 pores with a maximum perpendicular cross section of at least
31 about 13 Å. The second component of the system (the amine)
32 is used to expand the pore size of these materials to the
33 required 13 Å or greater size by expanding the micelle
34 created to form these mesoporous materials.

- 3 -

01 The mesoporous materials of the Beck patent are considered
02 very different from microporous materials, such as zeolites,
03 and are not currently considered to be zeolites.
04

05 SUMMARY OF THE INVENTION
06

07 Crystalline, microporous aluminosilicate molecular sieves
08 have been prepared in accordance with this invention using a
09 highly effective new method.
10

11 In accordance with this invention there is provided a method
12 for preparing a zeolite selected from the group consisting
13 of large pore zeolites, medium pore zeolites having
14 unidimensional channels, and small pore zeolites, said
15 method comprising:
16

- 17 A. forming an aqueous reaction mixture comprising (1) a
18 source of an oxide selected from silicon oxide,
19 germanium oxide and mixtures thereof; (2) a source of
20 an oxide selected from aluminum oxide, gallium oxide,
21 iron oxide, boron oxide, titanium oxide and mixtures
22 thereof; (3) a source of an alkali metal oxide; (4) an
23 amine component comprising at least one amine
24 containing one to eight carbon atoms, ammonium
25 hydroxide, and mixtures thereof, and (5) an organic
26 templating compound capable of forming said zeolite in
27 the presence of said amine, wherein said amine is
28 smaller than said organic templating compound; and
29
- 30 B. maintaining said aqueous mixture under sufficient
31 crystallization conditions until crystals are formed.
32

33 There is further provided in accordance with this invention
34 an improved method for preparing a zeolite selected from the

- 4 -

01 group consisting of large pore zeolites, medium pore
02 zeolites having unidimensional channels, and small pore
03 zeolites from source materials for said zeolite and an
04 organic templating compound, the improvement comprising
05 employing a mixture of (1) said organic templating compound,
06 and (2) an amine component comprising at least one amine
07 containing one to eight carbon atoms, ammonium hydroxide,
08 and mixtures thereof, said amine being smaller than said
09 organic templating compound and said organic templating
10 compound being capable of forming said zeolite in the
11 presence of said amine.

12

13 The present invention also provides these processes wherein
14 the organic templating compound is selected from the group
15 consisting of quaternary ammonium ions, cyclic amines and
16 polar adamantyl derivatives.

17

18 In a preferred embodiment, the present invention provides
19 these processes wherein the organic templating compound is
20 used in an amount less than that required to fill all of the
21 micropore volume of the zeolite.

22

23 In accordance with this invention, there is also provided a
24 zeolite having an as-synthesized molar composition in an
25 anhydrous state of $(0.02 \text{ to } 2.0)Q:(0.02 \text{ to } 1.0)Z:(0.1 \text{ to } 2.0)M_2O:W_2O_3:(10 \text{ to } 200)YO_2$, wherein M is an alkali metal
26 cation; W is selected from aluminum, gallium, iron, boron,
27 titanium and mixtures thereof; Y is selected from silicon,
28 germanium, and mixtures thereof; Z is an amine component
29 comprising at least one amine containing from one to eight
30 carbon atoms, ammonium hydroxide, and mixtures thereof; and
31 Q is an organic templating compound capable of forming the
32 zeolite in the presence of the amine.

34

- 5 -

01 Among other factors, the present invention is based on the
02 discovery that amines which could be used in the synthesis
03 of small and medium pore-sized zeolites can be used to
04 synthesize the large-pore zeolites, such as the zeolite
05 known as "Zeolite SSZ-25" or simply "SSZ-25", when used in
06 conjunction with a small amount of an organic templating
07 compound, such as an adamantane compound for SSZ-25. For
08 example, ZSM-5, a medium pore size, multidimensional
09 zeolite, was produced when the amine piperidine or
10 cyclopentylamine was used alone (see Table 4, Examples 7 and
11 9) as the templating compound. However, when a small amount
12 of an adamantyl quaternary ammonium ion was used in
13 combination with piperidine or cyclopentylamine, the
14 large-pore zeolite SSZ-25 resulted (see Table 4, Examples 6
15 and 8). This is particularly surprising since the amount of
16 the adamantyl quaternary ammonium ion that was used was
17 insufficient to cause significant growth of SSZ-25 if used
18 without other amines present.

19
20 It was wholly unexpected that amines such as isobutyl,
21 neopentyl, or monomethyl amine could be used in relatively
22 large quantities to produce zeolites such as SSZ-25 (see
23 Table 3, Examples 3 and 4). Use of amines containing from
24 one to eight carbon atoms provides significant cost savings
25 over the method of using, e.g., an adamantyl quaternary
26 ammonium ion as the sole source of organic component.
27 Additional manufacturing flexibility can be obtained, since
28 the process no longer depends on the availability of large
29 quantities of one particular amine.

30
31 In addition to these discoveries, it was found that polar
32 adamantyl derivatives could be substituted for the more
33 costly adamantyl quaternary ammonium ions being used in
34 combination with the amine component to prepare SSZ-25 (see

-6-

01 Examples 4, 5, 11, and 12), even though these polar
02 adamantyl derivatives do not result in crystallization of
03 SSZ-25 when used alone.. Therefore, the cost of making
04 SSZ-25 is further reduced.
05
06 Substantial reductions in growth time also occurred
07 unexpectedly when using the organic component mixture
08 comprising an amine component and an organic templating
09 compound. Growth times improved by a factor of from
10 approximately two to approximately five in some examples.
11 The commercial benefits of reduced plant construction cost
12 for a given production rate will be substantial.
13

14 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

15
16 The zeolites prepared in accordance with this invention are
17 microporous, crystalline materials which have a mole ratio
18 of an oxide selected from silicon oxide, germanium oxide,
19 and mixtures thereof to an oxide selected from aluminum
20 oxide, gallium oxide, iron oxide, boron oxide, titanium
21 oxide and mixtures thereof in the range of 10 to 200. These
22 zeolites further have a composition, as synthesized and in
23 the anhydrous state, in terms of mole ratios as follows:
24 $(0.02 \text{ to } 2.0)Q:(0.02 \text{ to } 1.0)Z:(0.1 \text{ to } 2.0)M_2O:W_2O_3:(10 \text{ to } 200)YO_2$, wherein M is an alkali metal cation; W is selected
25 from aluminum, gallium, iron, boron, titanium and mixtures
26 thereof; Y is selected from silicon, germanium, and mixtures
27 thereof; Z is an amine component comprising at least one
28 amine containing from one to eight carbon atoms, ammonium
29 hydroxide, and mixtures thereof; and Q is an organic
30 templating agent capable of forming the zeolite in the
31 presence of the amine.
32
33
34

- 7 -

01 The present invention involves a novel method for preparing
02 zeolites, comprising the preparation of an aqueous mixture
03 that contains sources of a minor quantity of an organic
04 templating compound capable of forming the desired zeolite,
05 a larger quantity of an amine component containing at least
06 one small amine ranging from 1 to 8 carbons, and/or ammonium
07 hydroxide, and preferably seeds of the desired zeolite.
08 Preferably, the amine component is an aliphatic or
09 cycloaliphatic amine containing no more than 8 carbon atoms
10 or mixtures of such compounds.

11
12 This invention provides considerable cost improvement and
13 flexibility in choice of organic components, and most
14 surprisingly, faster crystallization rates.

15
16 The present invention is useful in preparing large pore
17 zeolites having unidimensional channels, large pore zeolites
18 having multidimensional channels, medium pore zeolites
19 having unidimensional channels, small pore zeolites having
20 unidimensional channels and small pore zeolites having
21 multidimensional channels. As used herein, the term "large
22 pore zeolite" refers to zeolites which have \geq 12-ring
23 openings in their framework structure, the term "medium pore
24 zeolites" refers to zeolites which have 10-ring openings in
25 their framework structure, and the term "small pore
26 zeolites" refers to zeolites which have \leq 8-ring openings in
27 their framework structure. In addition, the term
28 "unidimensional" or "unidimensional channels" refers to the
29 fact that the pores in the zeolite form channels which are
30 essentially parallel and do not intersect, and the term
31 "multidimensional" or "multidimensional channels" refers to
32 the fact that the pores in the zeolite form channels which
33 do intersect each other.

34

- 8 -

01 The reaction mixtures used to prepare the zeolites by the
02 method of this invention may have a composition, in terms of
03 mole ratios, falling within the following ranges: $YO_2:W_2O_3$,
04 10:1 to 200:1; $M:YO_2$ 0.01:1 to 0.50:1; $OH:YO_2$ 0.01:1 to
05 0.60:1; Q/YO_2 0.02:1 to 1.00:1 and Z/YO_2 0.02:1 to 1.00:1,
06 where Y is selected from silicon, germanium, and mixtures
07 thereof; W is selected from aluminum, gallium, iron, boron,
08 titanium and mixtures thereof; M is an alkali metal cation;
09 Z is an amine component comprising at least one amine
10 containing from one to eight carbon atoms, ammonium
11 hydroxide, or mixtures thereof; and Q is an organic
12 templating compound capable of forming the zeolite in the
13 presence of the amine.

14

15 In some instances, the alkali metal cation level in the
16 reaction mixture should be carefully controlled. It has now
17 been discovered that alkali metal cation: SiO_2 mole ratios
18 much above 0.40 can favor the formation of the zeolites
19 ZSM-5 and mordenite. Indeed, it has been found that at high
20 alkali metal cation: SiO_2 mole ratios, these two zeolites can
21 be produced even in the absence of any organic templating
22 compound. Thus, in order to ensure that the desired zeolite
23 is produced, it is advisable to carefully control the alkali
24 metal cation content in the reaction mixture. To this end,
25 it may also be advisable to avoid using reagents such as
26 sodium and potassium silicates.

27

28 The present invention will now be described with respect to
29 one of the zeolites, SSZ-25, which can be made using the
30 method of this invention. It is understood that the other
31 zeolites which can be made using this method are made in
32 substantially the same way.

33

34

- 9 -

01 SSZ-25 has a mole ratio of an oxide selected from silicon
02 oxide, germanium oxide, and mixtures thereof to an oxide
03 selected from aluminum oxide, gallium oxide, iron oxide,
04 boron oxide, titanium oxide and mixtures thereof in the
05 range of 10 to 200, and having the X-ray diffraction lines
06 of Table 2 below. The zeolite further has a composition, as
07 synthesized and in the anhydrous state, in terms of mole
08 ratios of oxides as follows: $(0.02 \text{ to } 2.0)Q:(0.20 \text{ to } 1.0)Z:$
09 $(0.1 \text{ to } 2.0)M_2O:W_2O_3:(10 \text{ to } 200)YO_2$, wherein M is an
10 alkali metal cation; W is selected from aluminum, gallium,
11 iron, boron, titanium and mixtures thereof; Y is selected
12 from silicon, germanium, and mixtures thereof; and Q is an
13 adamantane compound comprising at least one compound chosen
14 from the group consisting of adamantane quaternary ammonium
15 ions and polar adamantyl derivatives, and Z is an amine
16 component comprising at least one amine chosen from amines
17 containing from one to eight carbon atoms. SSZ-25 zeolites
18 can have a $YO_2:W_2O_3$ mole ratio in the range of about 10 to
19 200. As prepared, the silica to alumina mole ratio is
20 typically in the range of about 15:1 to about 100:1. Higher
21 mole ratios can be obtained by treating the zeolite with
22 chelating agents or acids to extract aluminum from the
23 zeolite lattice. The silica to alumina mole ratio can also
24 be increased by using silicon and carbon halides and other
25 similar compounds. Preferably, SSZ-25 is an aluminosilicate
26 wherein W is aluminum and Y is silicon.
27

28 SSZ-25 zeolites, as synthesized in the presence of adamantyl
29 compounds, have crystalline structures with the X-ray powder
30 diffraction patterns containing the following characteristic
31 lines:
32
33
34

-10-

TABLE 1(a)			
	<u>2 θ</u>	<u>d/n</u>	<u>Int.</u>
01			
02			
03	5.0	17.7	2 Br
04	6.92	12.77	28
05	7.06	12.52	26
06	7.87	11.23	21
07	8.78	10.07	1
08	9.31	9.5	5
09	9.93	8.91	42
10	12.47	7.10	2
11	12.79	6.92	7
12	14.00	6.33	22
13	14.21	6.23	24
14	14.67	6.04	10
15	15.87	5.58	15
16	17.65	5.02	2
17	18.89	4.70	5
18	20.02	4.44	13
19	20.15	4.41	12
20	21.02	4.23	9
21	21.48	4.14	11
22	21.75	4.09	16
23	22.28	3.99	14
24	22.60	3.93	33
25	23.60	3.77	25
26	24.60	3.62	6
27	24.84	3.58	10
28	25.10	3.55	11
29	25.88	3.44	67
30	26.83	3.32	15
31	27.64	3.23	20
32	28.47	3.14	16
33	29.00	3.08	1
34	29.54	3.02	3

-11-

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TABLE 1(a) (cont.)

31.42	2.85	3
32.15	2.78	4
33.23	2.70	7
34.22	2.62	3

-12-

TABLE 1(b)

	<u>2 θ</u>	<u>d/n</u>	<u>Int.</u>
01			
02			
03	7.08	12.49	40
04	7.89	11.21	25
05	8.89	9.95	6
06	9.91	8.93	46
07	11.43	7.74	1
08	12.80	6.92	9
09	14.00	6.33	Sh
10	14.22	6.23	35
11	14.68	6.03	13
12	15.87	5.58	17
13	17.75	5.00	2
14	18.95	4.68	6
15	19.38	4.58	10
16	19.58	4.53	9
17	20.05	4.43	13
18	20.15	4.41	Sh
19	21.00	4.23	5
20	21.49	4.13	10
21	21.78	4.08	17
22	22.30	3.99	Sh
23	22.58	3.94	35
24	23.59	3.77	25
25	24.55	3.63	Sh
26	24.82	3.59	10
27	25.07	3.55	5
28	25.85	3.45	68
29	26.48	3.37	3
30	26.85	3.32	16
31	27.64	3.23	19
32	28.46	3.14	14
33			
34			

-13-

01 TABLE 1(b) (cont.)

02	28.98	3.08	3
03	29.60	3.02	4
04	31.42	2.85	4
05	32.18	2.78	5
06	33.21	2.70	7
07	34.22	2.62	2

08
09 As can be seen in Tables 1(a) and 1(b), X-ray diffraction
10 patterns of the as synthesized SSZ-25 will vary.

11
12 After calcination, the SSZ-25 zeolites have a crystalline
13 structure whose X-ray powder diffraction pattern shows the
14 following characteristic lines as indicated in Table 2
15 below:

16
17 TABLE 2

19	<u>2 θ</u>	<u>d/n</u>	<u>I/I₀</u>
20	3.4	25.5	17
21	7.19	12.30	100
22	8.04	11.00	55
23	10.06	8.78	63
24	14.35	6.17	40
25	16.06	5.51	17
26	22.77	3.90	38
27	23.80	3.74	20
28	26.08	3.417	65

29
30 The X-ray powder diffraction patterns were determined by
31 standard techniques. The radiation was the K-alpha/doublet
32 of copper and a scintillation counter spectrometer with a
33 strip-chart pen recorder was used. The peak heights I and
34 the positions, as a function of 2 θ where θ is the Bragg

-14-

01 angle, were read from the spectrometer chart. From these
02 measured values, the relative intensities, $100I/I_0$, where I_0
03 is the intensity of the strongest line or peak, and d , the
04 interplanar spacing in Angstroms corresponding to the
05 recorded lines, can be calculated. Variations in the
06 diffraction pattern can result from variations in the
07 organic component used in the preparation and from
08 variations in the silica-to-alumina mole ratio from sample
09 to sample. The zeolite produced by exchanging the metal or
10 other cations present in the zeolite with various other
11 cations yields a similar diffraction pattern, although there
12 can be shifts in interplanar spacing as well as variations
13 in relative intensity. Calcination can also cause shifts in
14 the X-ray diffraction pattern. Notwithstanding these
15 perturbations, the basic crystal lattice structure remains
16 unchanged.

17

18 Zeolites can be suitably prepared from an aqueous solution
19 containing sources of an alkali metal oxide, an organic
20 component mixture, an oxide of aluminum, gallium, iron,
21 boron, titanium or mixtures thereof, and an oxide of silicon
22 or germanium, or mixture of the two. The reaction mixture
23 should have a composition in terms of mole ratios falling
24 within the following ranges:

25

26		<u>Broad</u>	<u>Preferred</u>
27	M/YO ₂	0.01-0.50	0.10-0.20
28	OH ⁻ /YO ₂	0.01-0.60	0.10-0.30
29	H ₂ O/YO ₂	10-120	20-50
30	Q/YO ₂	0.02-1.00	0.02-0.10
31	YO ₂ /W ₂ O ₃	10-200	15-120
32	Z/YO ₂	0.05-1.00	0.20-0.40

33

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-15-

01 where M is an alkali metal, preferably sodium or potassium;
02 Y is silicon, germanium, or both; Q is an adamantane-
03 component comprising at least one compound chosen from the
04 group consisting of adamantane quaternary ammonium ions and
05 polar adamantyl derivatives, Z is an amine component
06 comprising at least one amine chosen from amines containing
07 from one to eight carbon atoms, ammonium hydroxide and
08 mixtures thereof; and W is aluminum, gallium, iron, boron,
09 titanium or mixtures thereof.

10

11 The reaction mixture can also be seeded with as-made zeolite
12 crystals both to direct and accelerate the crystallization,
13 as well as to minimize the formation of undesired
14 aluminosilicate contaminants.

15

16 By "polar adamantyl derivative" is meant adamantyl compounds
17 which contain either (a) a nitrogen atom that can bear a
18 lone pair of electrons or an electropositive charge, or
19 (b) an hydroxyl substituent. By "adamantane quaternary
20 ammonium ions" is meant adamantane materials containing a
21 nitrogen atom which is chemically bonded to four
22 substituents, at least three of which are methyl groups and
23 at least one of which is an adamantyl compound. By an
24 "adamantane compound" or "adamantane component" is meant a
25 composition comprising at least one compound chosen from the
26 group consisting of adamantane quaternary ammonium ions and
27 polar adamantyl derivatives. By "amine component" is meant
28 at least one amine chosen from the group of amines having
29 from one to eight carbon atoms, ammonium hydroxide or
30 mixtures thereof. Preferably, the amine is an aliphatic or
31 cycloaliphatic amine containing no more than 8 carbon atoms
32 and mixtures thereof. By "organic component mixture" is
33 meant a mixture comprising the organic templating compound
34 and the amine component. By "seed material" is meant a

-16-

01 material which reduces growth times of the zeolite crystals.
02 One example of a seed material for SSZ-25 is as-made-SSZ-25.
03 By "SSZ-25" is meant a material consisting substantially of
04 the crystalline material with an X-ray diffraction pattern
05 corresponding substantially to that of Table 2 after
06 calcination of the as-made material.

07

08 The reaction mixture is prepared using standard zeolitic
09 preparation techniques. Typical sources of aluminum oxide
10 for the reaction mixture include aluminates, alumina,
11 hydrated aluminum hydroxides, and aluminum compounds such as
12 AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$. Typical sources of silicon oxide include
13 silica hydrogel, silicic acid, colloidal silica, tetraalkyl
14 orthosilicates, silica hydroxides, and fumed silicas.
15 Gallium, iron, boron, titanium and germanium can be added in
16 forms corresponding to their aluminum and silicon
17 counterparts. Trivalent elements stabilized on silica
18 colloids are also useful reagents.

19

20

21 The organic component mixture used to prepare SSZ-25 may
22 contain adamantane quaternary ammonium ions. The adamantane
23 quaternary ammonium ions are derived from a compound of the
24 formula:

25

26

27

28

29

30

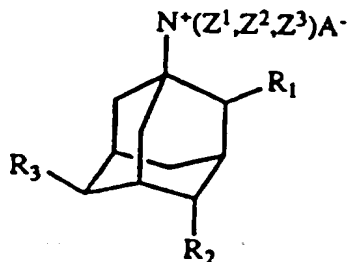
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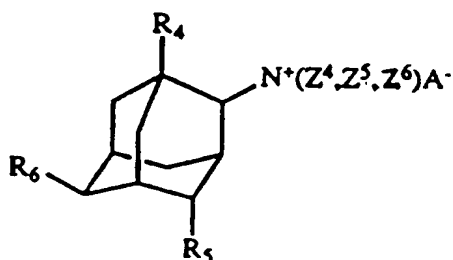
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-17-



(I)

wherein each of Z^1 , Z^2 and Z^3 independently is lower alkyl and most preferably methyl; A^\ominus is an anion which is not detrimental to the formation of the zeolite; and each of R^1 , R^2 and R^3 independently is hydrogen, or lower alkyl and most preferably hydrogen; and



(II)

wherein each of R^4 , R^5 and R^6 independently is hydrogen or lower alkyl; and most preferably hydrogen; each of Z^4 , Z^5 and Z^6 independently is lower alkyl and most preferably methyl; and A^\ominus is an anion which is not detrimental to the formation

-18-

01 of the zeolite. Mixtures of compounds having formula (I)
02 and/or (II) can also be used. By "lower alkyl" is meant
03 alkyl of from about 1 to 5 carbon atoms.

04
05 A^o is an anion which is not detrimental to the formation of
06 the zeolite. Representative of the anions include halide,
07 e.g., fluoride, chloride, bromide and iodide, hydroxide,
08 acetate, sulfate, carboxylate, etc. Hydroxide is the most
09 preferred anion. It may be beneficial, for example, to
10 ion-exchange the halide for hydroxide ion, thereby reducing
11 the alkali metal hydroxide quantity required.

12

13 The adamantane quaternary ammonium compounds are prepared by
14 methods known in the art.

15

16 The organic component mixture used to prepare SSZ-25 may
17 contain a polar adamantyl derivative. The polar adamantyl
18 derivative is commercially available and includes compounds
19 such as 1-adamantanamine, 2-adamantanamine, 1-aminomethyl
20 adamantane, 1-adamantanol, 2-adamantanol and mixtures of
21 such compounds. Use of the polar adamantyl derivative
22 instead of adamantane quaternary ammonium ions permits a
23 reduction of production cost when making SSZ-25.

24

25 The organic component mixture used to prepare SSZ-25 also
26 contains an amine component comprising at least one amine
27 chosen from amines containing from one to eight carbon
28 atoms, ammonium hydroxide and mixtures thereof. These
29 amines are smaller than the organic templating compound used
30 to prepare the zeolite. As used herein, the term "smaller",
31 when used with respect to the amine component, means that
32 the amine is lower in molecular weight than the organic
33 templating compound and typically is no larger physically
34 than the organic templating compound. Non-exclusive

-19-

01 examples of these amines include isopropylamine, isobutyl
02 amine, n-butylamine, piperidine, 4-methylpiperidine,
03 cyclohexylamine, 1,1,3,3-tetramethyl butyl amine and
04 cyclopentylamine and mixtures of such amines.
05

06 Use of these amines permits a reduction in the amount of the
07 adamantane compound (or other organic templating compound)
08 used, and significant cost savings result. In fact, it has
09 quite surprisingly been found that, by using the amine
10 component of the present invention, the amount of organic
11 templating compound can be reduced to a level below that
12 which is required to fill the micropore volume of the
13 zeolite. In addition, use of these amines unexpectedly
14 promotes faster growth times when used in combination with
15 seed material.
16

17 In the previous SSZ-25 synthesis that relied completely on
18 the quaternized adamantammonium derivative in larger
19 quantity, a minimum of usually 160 hours was required to
20 obtain the crystallized SSZ-25. By using an adamantane
21 compound in conjunction with an amine component and seed
22 material, crystallization periods of approximately 50 hours
23 have been observed. A significant cost reduction in
24 commercial use will occur as a result of the substantial
25 reduction in crystallization period, since less equipment
26 time is needed to grow SSZ-25 for a given production rate.
27

28 The reaction mixture used to prepare SSZ-25 can be seeded
29 with material such as SSZ-25 crystals both to direct, and
30 accelerate the crystallization, as well as to minimize the
31 formation of undesired aluminosilicate contaminants.
32
33
34

-20-

01 The preferred reaction mixture for making SSZ-25 comprises
02 1-adamantanamine, isobutylamine, and SSZ-25 seeds as
03 formulated in Example 17.

04

05 The reaction mixture is maintained at an elevated
06 temperature until the crystals of the zeolite are formed.
07 The temperatures during the hydrothermal crystallization
08 step are typically maintained from about 140°C to about
09 200°C, preferably from about 160°C to about 180°C, and most
10 preferably from about 170°C to about 180°C. The
11 crystallization period is typically greater than 1 day and
12 preferably from about 2 days to about 5 days.

13

14 The hydrothermal crystallization is conducted under pressure
15 and usually in an autoclave so that the reaction mixture is
16 subject to autogenous pressure. The reaction mixture can be
17 stirred during crystallization. During the hydrothermal
18 crystallization step, the zeolite crystals can be allowed to
19 nucleate spontaneously from the reaction mixture.

20

21 Once the zeolite crystals have formed, the solid product is
22 separated from the reaction mixture by standard mechanical
23 separation techniques such as filtration. The crystals are
24 water-washed and then dried, e.g., at 90°C to 120°C for from
25 8 to 24 hours, to obtain the as-synthesized zeolite
26 crystals. The drying step can be performed at atmospheric
27 or subatmospheric pressures.

28

29 The synthetic zeolites can be used as synthesized or can be
30 thermally treated. By "thermal treatment" is meant heating
31 to a temperature from about 200°C to about 820°C, either
32 with or without the presence of steam. Usually, it is
33 desirable to remove the alkali metal cation by ion exchange
34 and replace it with hydrogen, ammonium, or any desired metal

-21-

01 ion. Thermal treatment including steam helps to stabilize
02 the crystalline lattice from attack by acids. The zeolite
03 can be leached with chelating agents, e.g., EDTA or dilute
04 acid solutions, to increase the silica:alumina mole ratio.
05 The zeolite can be used in intimate combination with
06 hydrogenating components, such as tungsten, vanadium,
07 molybdenum, rhenium, nickel, cobalt, chromium, manganese, or
08 a noble metal, such as palladium or platinum, for those
09 applications in which a hydrogenation-dehydrogenation
10 function is desired. Typical replacing cations can include
11 metal cations, e.g., rare earth, Group IIA and Group VIII
12 metals, as well as their mixtures. Of the replacing
13 metallic cations, cations of metals such as rare earth, Mn,
14 Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe and Co are
15 particularly preferred.

16
17 The hydrogen, ammonium, and metal components can be
18 exchanged into the zeolite. The zeolite can also be
19 impregnated with the metals, or the metals can be physically
20 intimately admixed with the zeolite using standard methods
21 known to the art. Also, the metals can be occluded in the
22 crystal lattice by having the desired metals present as ions
23 in the reaction mixture from which the zeolite is prepared.

24
25 Typical ion exchange techniques involve contacting the
26 synthetic zeolite with a solution containing a salt of the
27 desired replacing cation or cations. Although a wide
28 variety of salts can be employed, chlorides and other
29 halides, nitrates, acetates, and sulfates are particularly
30 preferred. Representative ion exchange techniques are
31 disclosed in a wide variety of patents including U.S. Patent
32 Nos. 3,140,249, issued July 7, 1964 to Plank et al.,
33 3,140,251, issued July 7, 1964 to Plank et al., and
34 3,140,253, issued July 7, 1964 to Plank et al. Ion exchange

-22-

01 can take place either before or after the zeolite is
02 calcined.

03

04 Following contact with the salt solution of the desired
05 replacing cation, the zeolite is typically washed with water
06 and dried at temperatures ranging from 65°C to about 315°C.
07 After washing, the zeolite can be calcined in air or inert
08 gas at temperatures ranging from about 200°C to 820°C for
09 periods of time ranging from 1 to 48 hours, or more, to
10 produce a catalytically active product especially useful in
11 hydrocarbon conversion processes.

12

13 Regardless of cations present in the synthesized form of the
14 zeolite, the spatial arrangement of the atoms which form the
15 basic crystal lattice of the zeolite remains essentially
16 unchanged. The exchange of cations has little, if any,
17 effect on the zeolite lattice structures.

18

19 The zeolites can be formed into a wide variety of physical
20 shapes. Generally speaking, the zeolite can be in the form
21 of a powder, a granule, or a molded product, such as
22 extrudate having particle size sufficient to pass through a
23 2-mesh (Tyler) screen and be retained on a 400-mesh (Tyler)
24 screen. In cases where the catalyst is molded, such as by
25 extrusion with an organic binder, the aluminosilicate can be
26 extruded before drying, or dried or partially dried and then
27 extruded. The zeolite can be composited with other
28 materials resistant to the temperatures and other conditions
29 employed in organic conversion processes. By "matrix
30 material" is meant other materials with which the zeolite is
31 combined to make catalyst particles. Such matrix materials
32 may include active and inactive materials and synthetic or
33 naturally occurring zeolites as well as inorganic materials
34 such as clays, silica and metal oxides. The latter may

-23-

01 occur naturally or may be in the form of gelatinous
02 precipitates, sols, or gels, including mixtures of silica
03 and metal oxides. Use of an active material in conjunction
04 with the synthetic zeolite, i.e., combined with it, tends to
05 improve the conversion and selectivity of the catalyst in
06 certain organic conversion processes. Inactive materials
07 can suitably serve as diluents to control the amount of
08 conversion in a given process so that products can be
09 obtained economically without using other means for
10 controlling the rate of reaction. Catalysts produced with
11 zeolites or other components incorporated therein may be
12 subject to further ion exchange steps, metal inclusion,
13 thermal treatment, and other processing steps as previously
14 discussed for the zeolite alone.

15
16 Frequently, zeolite materials have been incorporated into
17 naturally occurring clays, e.g., bentonite and kaolin.
18 These materials, i.e., clays, oxides, etc., function, in
19 part, as binders for the catalyst. It is desirable to
20 provide a catalyst having good crush strength, because in
21 petroleum refining the catalyst is often subjected to rough
22 handling. This tends to break the catalyst down into
23 powders which cause problems in processing.

24
25 Naturally occurring clays which can be composited with the
26 synthetic zeolites of this invention include the
27 montmorillonite and kaolin families, which families include
28 the sub-bentonites and the kaolins commonly known as Dixie,
29 McNamee, Georgia and Florida clays or others in which the
30 main mineral constituent is halloysite, kaolinite, dickite,
31 nacrite, or anauxite. Fibrous clays such as sepiolite and
32 attapulgite can also be used as supports. Such clays can be
33 used in the raw state as originally mined or can be
34

-24-

01 initially subjected to calcination, acid treatment or
02 chemical modification.

03

04 In addition to the foregoing materials, the zeolites can be
05 composited with porous matrix materials and mixtures of
06 matrix materials such as silica, alumina, titania, magnesia,
07 silica:alumina, silica-magnesia, silica-zirconia,
08 silica-thoria, silica-beryllia, silica-titania,
09 titania-zirconia as well as ternary compositions such as
10 silica-alumina-thoria, silica-alumina-zirconia,
11 silica-alumina-magnesia and silica-magnesia-zirconia. The
12 matrix can be in the form of a cogel.

13

14 The zeolites can also be composited with other zeolites such
15 as synthetic and natural faujasites (e.g., X and Y),
16 erionites, and mordenites. They can also be composited with
17 purely synthetic zeolites such as those of the ZSM series.
18 The combination of zeolites can also be composited in a
19 porous inorganic matrix.

20

21 Zeolites are useful in hydrocarbon conversion reactions.
22 Examples of these uses are described in U.S. Patent
23 No. 4,826,667, issued May 2, 1989 to Zones et al., which is
24 incorporated herein by reference.

25

26 While the foregoing description has involved primarily the
27 preparation of SSZ-25, it should be emphasized that other
28 zeolites can be prepared using the method of this invention.
29 For example, the zeolites known as SSZ-32, SSZ-28, EU-1,
30 SSZ-35, ferrierite, ZSM-12 and ZSM-22 type structures have
31 been successfully prepared in accordance with this
32 invention. When it is desired to prepare these or other
33 zeolites by the method of this invention, an organic

34

-25-

01 templating compound capable of producing the desired zeolite
02 in the presence of the amine component is employed.
03

04 In general, the mole ratios of the components of the
05 reaction mixtures used to prepare these zeolites will be the
06 same as, or very similar to, those described above with
07 respect to SSZ-25, except, of course that the structure of
08 the organic templating compound (Q) used will depend upon
09 the zeolite desired to be made. Also, the composition of
10 the reaction mixture may vary slightly depending upon the
11 zeolite desired to be made.

12

13 Zeolite SSZ-32

14

15 To prepare SSZ-32, an N-lower alkyl-N'-isopropylimidazolium
16 cation may be used as the organic templating compound.
17 These compounds have the general formula:

18

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28 wherein R is lower alkyl containing 1 to 5 carbon atoms
29 (preferably methyl or isopropyl) and A⁻ is an anion which is
30 not detrimental to the formation of the zeolite.

31 Representative anions include halogens, e.g., fluoride,
32 chloride, bromide and iodide, hydroxide, acetate, sulfate,
33 carboxylate, and the like. Hydroxide is the most preferred
34 anion.



-26-

01 The preferred N-lower alkyl-N'-isopropylimidazolium cations
 02 are N,N'-diisopropylimidazolium cation and N-methyl-N'
 03 isopropylimidazolium cation.

04

05 Another type of organic template which can be employed to
 06 prepare SSZ-32 are N,N,N-trialkyl-1,1,3,3-tetraalkylbutyl
 07 ammonium cations, which have the general formula:

08

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where R and A are as defined above for formula III.
 Preferably, R is methyl.

The as-made SSZ-32 zeolites have a crystalline structure
 whose X-ray powder diffraction pattern shows the following
 characteristic lines as indicated in Table A below:

- 27 -

TABLE A

	<u>2Theta</u>	<u>d/n</u>	<u>I/I₀</u>
01			
02			
03			
04	8.04	10.99	30.2
05	8.81	10.03	12.6
06	11.30	7.82	23.1
07	18.08	4.90	8.0
08	19.56	4.53	61.2
09	20.81	4.26	65.1
10	22.75	3.90	100.0
11	23.89	3.72	85.6
12	24.59	3.62	34.9
13	25.16	3.53	21.9
14	25.91	3.43	41.8
15	26.89	3.31	7.2
16	28.13	3.17	11.5
17	29.30	3.04	5.9
18	31.48	2.84	6.0

ZSM-22 type zeolite

19

20 The organic templating compounds which may be used to
 21 prepare ZSM-22 type structures include imidazole salts
 22 characterized by the following formula:

23

24

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A⁻

(IV)

wherein X¹ and X² independently represent a linear alkyl
 group containing from 1 to about 10 carbon atoms and A^o

-28-

01 represents an anion which is not detrimental to the
02 formation of the desired molecular sieve, such as those
03 described above for formula (III).

04

05 The alkyl substitutions on the nitrogen atoms of the
06 imidazole ring are any straight chain alkyl group having
07 from 1 to about 10 carbon atoms. Thus, this moiety includes
08 methyl, ethyl, propyl, n-butyl, as well as linear pentyl,
09 hexyl, heptyl, octyl, nonyl, and decyl groups.

10

11 ZSM-22 type zeolites can also be prepared using piperidine
12 derivatives as the organic templating compound. A preferred
13 piperidine derivative is 2,6-dimethylpiperidine.

14

15 The as-made ZSM-22 zeolites have a crystalline structure
16 whose X-ray powder diffraction pattern shows the following
17 characteristic lines as indicated in Table B below:

18

19

TABLE B

20

21	<u>2Theta</u>	<u>d/n</u>	<u>I/I₀</u>
22	8.13	10.87	37.7
23	10.15	8.70	4.0
24	12.72	6.95	18.6
25	16.51	5.36	2.6
26	19.36	4.58	3.0
27	20.28	4.38	100.0
28	24.11	3.69	75.3
29	24.53	3.63	75.2
30	25.64	3.47	63.9

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-29-

01 Zeolite SSZ-28

02

03 To prepare SSZ-28, sources of an N,N-dimethyl-tropinium or
04 N,N-dimethyl-3-azonium bicyclo[3.2.2]nonane cation may be
05 used as the organic templating compound.

06

07 The as-made SSZ-28 zeolites have a crystalline structure
08 whose X-ray powder diffraction pattern shows the following
09 characteristic lines as indicated in Table C below:

10

TABLE C

11

12	2Theta	d/n	I/I ₀
13	7.62	11.58	11.0
14	11.28	7.83	7.1
15	12.94	6.84	9.6
16	15.36	5.76	64.7
17	17.09	5.18	100.0
18	18.24	4.86	32.0
18	18.80	4.71	31.8
19	19.66	4.51	40.1
20	21.40	4.14	26.0
21	24.85	3.58	12.1
22	26.18	3.40	64.5
23	26.49	3.40	28.0
24	26.85	3.32	28.6
24	28.14	3.17	13.7
25	29.75	3.00	13.0

26

27 Zeolite EU-1

28

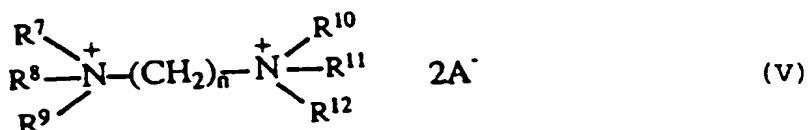
29 The organic templating compounds useful in preparing EU-1
30 are alkylated derivatives of a polymethylene α - ω diamine
31 having the formula:

32

33

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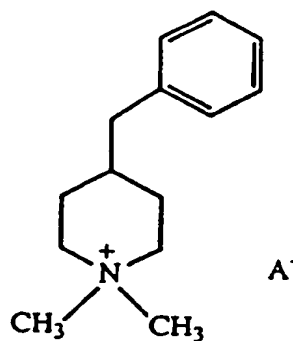


wherein n is in the range from 3 to 12 and R^7 to R^{12} which may be the same or different, can be alkyl or hydroxyalkyl groups, containing from 1 to 8 carbon atoms and up to five of the groups R^7 - R^{12} can be hydrogen, and A^- represents an anion which is not detrimental to the formation of the desired zeolite, such as those described above for formula (III).

Preferred alkylated polymethylene diamine derivatives include alkylated hexamethylene diamines, especially methylated hexamethylene diamines, for example 1,6 N,N,N,N',N',N'-hexamethyl hexamethylene diammonium salts (e.g., halide, hydroxide, sulphate, silicate, aluminate).

Other organic templating compounds which can be used to prepare EU-1 in accordance with the present invention are 4-benzyl-N,N-dimethylpiperidinium compounds, which have the following structure:

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where A⁻ represents an anion which is not detrimental to the formation of the desired molecular sieve, such as those described above for formula (III).

The as-made EU-1 zeolites have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table D below:

- 32 -

TABLE D

	2Theta	d/n	I/I _o
04	7.92	11.15	48.3
05	8.70	10.15	21.5
06	9.06	9.75	6.0
07	12.87	6.87	2.3
08	19.04	4.65	39.7
09	20.53	4.32	100.0
10	22.15	4.01	61.8
11	23.26	3.82	31.8
12	23.94	3.71	20.0
13	25.97	3.43	9.3
14	26.52	3.36	9.4
15	27.29	3.26	34.8

15

Zeolite SSZ-35

17

18 SSZ-35 can be prepared in accordance with the present
19 invention using a polycyclic compound having the following
20 formula as the organic templating compound:

21

22

23

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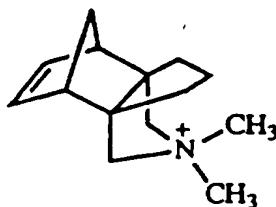
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27

28

29 where A⁻ is an anion which is not detrimental to the
30 formation of the desired zeolite, such as those described
31 above for formula (III). Another organic templating
32 compound which may be used to prepare SSZ-35 in accordance
33 with this invention is N-ethyl-N-methyl-9-

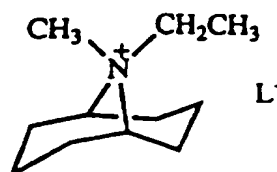
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(VI)

- 33 -

01 azoniabicyclo[3.3.1]nonane which has the following
02 structure:



12 where L⁻ is an anion which is not detrimental to the
13 production of the molecular sieve, such as those described
14 above for formula (III).

15 The anion for the salt may be essentially any anion such as
16 halide or hydroxide which is not detrimental to the
17 formation of the molecular sieve. As used herein, "halide"
18 refers to the halogen anions particularly fluorine,
19 chlorine, bromine, iodine, and combinations thereof. Thus,
20 representative anions include hydroxide, acetate, sulfate,
21 carboxylate, tetrafluoroborate, and halides, such as
22 fluoride, chloride, bromide and iodide. Hydroxide and
23 iodide are particularly preferred as anions.
24

25 The N-ethyl-N-methyl-9-azabicyclo[3.3.1]nonane templating
26 compound used in making SSZ-35 is a conformationally
27 constrained organic molecule. Altering the structure of
28 this relatively rigid molecule can lead to a change in the
29 molecular sieve obtained, presumably due to the differing
30 steric demands of each template. However, increasing the
31 steric requirements of the template may lead to a decrease
32 in crystallization rate as well as a decrease in template
33 solubility in the reaction mixture. If the template is not
34

-34-

01 sufficiently soluble, or if the template has particularly
02 bulky substituent groups, it may be difficult to form
03 crystals in the reaction mixture. Addition of a surfactant
04 to the reaction mixture may help to solubilize the template.

05

06 The N-ethyl-N-methyl-9-azabicyclo[3.3.1]nonane templating
07 compound may be synthesized by conventional techniques. In
08 general, this template can be prepared in an efficient
09 manner by condensing glutardialdehyde with a primary amine
10 and acetone-dicarboxylic acid, all of which are readily
11 available, inexpensive reagents. The intermediate formed is
12 the 2,4-dicarboxy-3-keto-9-aza-bicyclononane, a
13 di- β -ketoester which is easily decarboxylated upon treatment
14 with acid. The 3-keto-moiety is removed by a classic
15 Wolff-Kishner reduction (hydrazine, triethylene glycol,
16 potassium hydroxide), and the desired quaternary ammonium
17 salt is obtained by reaction of the resulting amine with an
18 alkyl halide. Following purification by recrystallization,
19 the halide salt can be ion-exchanged to the corresponding
20 hydroxide salt using an ion-exchange resin.

21

22 The as-made SSZ-35 zeolites have a crystalline structure
23 whose X-ray powder diffraction pattern shows the following
24 characteristic lines as indicated in Table E below:

25

26

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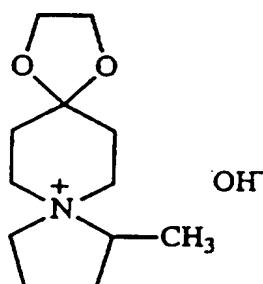
- 35 -

TABLE E

	<u>2Theta</u>	<u>d/n</u>	<u>I/I₀</u>
01			
02			
03			
04	7.99	11.05	100.0
05	9.65	9.16	7.4
06	15.37	5.76	17.0
07	18.88	4.69	43.7
08	19.32	4.59	62.6
09	19.82	4.48	30.1
10	21.60	4.11	17.8
11	22.80	3.89	20.8
12	25.68	3.47	29.6
13	27.41	3.25	27.3
14	29.20	3.06	17.6

Zeolite ZSM-12

Zeolite ZSM-12 can be prepared in accordance with this invention using a heterocyclic compound having the following formula as the organic templating compound:



(VIII)

wherein L⁻ is an anion which is not detrimental to the formation of the ZSM-12.

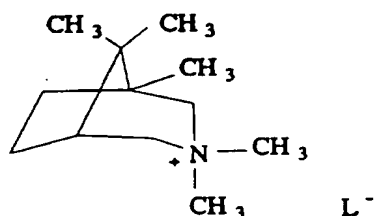
The as-made ZSM-12 zeolite has a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table F below:

- 36 -

TABLE F

	2Theta	d	I/I _o x 100
01			
02			
03	7.43	11.05	24.4
04	8.70	10.15	9.5
05	18.87	4.70	15.6
06	19.90	4.46	6.9
07	20.75	4.28	100.0
08	22.93	3.88	52.8
09	26.26	3.39	13.3
10	27.82	3.20	4.8
11	35.41	2.53	11.4

Another surprising aspect of this invention is that, when some organic templating compounds are used in combination with the amine component of this invention, a different zeolite structure is made than that which would be obtained in the absence of the amine component. For example, SSZ-35 has been made from organic templating compounds which are salts of 1,3,3,8,8-pentamethyl-3-azonia[3.2.1]octane. These compounds have a molecular structure of the general formula:



wherein L⁻ is an anion which is not detrimental to the formation of the zeolite. However, when these organic templating compounds are used in combination with the amine component of this invention, the resulting zeolite is SSZ-25.

-37-

01 Each organocation of this 1,3,3,8,8-pentamethyl-3-
02 azonia[3.2.1]octane family has a charged quaternary ammonium
03 heteroatom and two rings, one of which includes the
04 quaternary ammonium heteroatom as a bridging unit. The
05 anion for the salt may be essentially any anion such as
06 halide or hydroxide which is not detrimental to the
07 formation of the molecular sieve. As used herein, "halide"
08 refers to the halogen anions particularly fluorine,
09 chlorine, bromine, iodine, and combinations thereof. Thus,
10 representative anions include hydroxide, acetate, sulfate,
11 carboxylate, tetrafluoroborate, and halides such as
12 fluoride, chloride, bromide, and iodide. Hydroxide and
13 iodide are particularly preferred as anions.

14
15 Many of the organocation salts which have been disclosed in
16 the prior art for use as templates for molecular sieve
17 synthesis are conformationally flexible. These molecules
18 can adopt many conformations in aqueous solution, and
19 several templates can give rise to a single crystalline
20 product. In contrast, the 1,3,3,8,8-pentamethyl-3-
21 azoniabicyclo[3.2.1]octane templating compounds described
22 above used to make SSZ-25 are conformationally constrained
23 organic molecules.

24
25 These 1,3,3,8,8-pentamethyl-3-azoniabicyclo[3.2.1]octane
26 compounds can be prepared by converting camphoric anhydride
27 to the corresponding N-methyl imide using methyl amine. The
28 imide can be reduced to N-methylcamphidine upon reduction
29 with lithium aluminum hydride in ether, and the desired
30 quaternary ammonium salt obtained by treatment with methyl
31 iodide. Following purification by recrystallization, the
32 halide salt can be ion-exchanged to the corresponding
33 hydroxide salt using an ion-exchange resin.

34

- 38 -

EXAMPLESExample 1Preparation of N,N,N-Trimethyl-1-adamantanammonium Hydroxide
(Template A)

Ten (10) grams of 1-adamantanamine (Aldrich) was dissolved in a mixture of 29 gms tributylamine and 60 mls dimethylformamide. The mixture was chilled in an ice bath.

28.4 Grams of methyl iodide were added dropwise to the chilled solution with continuous stirring. After several hours, crystals appear. The reaction was continued overnight and allowed to come to room temperature. The crystals were filtered and washed with tetrahydrofuran and then diethyl ether before vacuum drying. Additional product was obtained by adding enough diethyl ether to the reaction filtrate to produce two phases and then with vigorous stirring acetone was added until the solution just became one phase. Continued stirring produced crystallization at which time the solution can be chilled to induce further crystallization. The product has a melting point near 300°C (decomp.) and the elemental analyses and NMR are consistent with the known structure. The vacuum-dried iodide salt was then ion-exchanged with ion-exchange resin AG 1X8 (in molar excess) to the hydroxide form. The exchange was performed over a column or more preferably by overnight stirring of the resin beads and the iodide salt in an aqueous solution designed to give about a 0.5 molar solution of the organic hydroxide. This produces Template A.

-39-

01 Example 2
02 Preparation of N,N,N-Trimethyl-2-adamantanammonium Hydroxide
03 (Template B)
04

05 Five (5) grams of 2-adamantanone (Aldrich Chemical Co.) was
06 mixed with 2.63 gms of formic acid (88%) and 4.5 gms of
07 dimethyl formamide. The mixture was then heated in a
08 pressure vessel for 16 hours at 190°C. Care should be taken
09 to anticipate the increase in pressure the reaction
10 experiences due to CO₂ evolution. The reaction was
11 conveniently carried out in a Parr 4748 reactor with teflon
12 liner. The workup consists of extracting N,N-dimethyl-2-
13 adamantanamine from a basic (pH=12) aqueous solution with
14 diethyl ether. The various extracts were dried with Na₂SO₄,
15 the solvent removed and the product taken up in ethyl
16 acetate. An excess of methyl iodide was added to a cooled
17 solution which was then stirred at room temperature for
18 several days. The crystals were collected and washed with
19 diethyl ether to give N,N,N-trimethyl-2-adamantanammonium
20 iodide. The product is checked by microanalysis for C, H,
21 and N. The conversion to the hydroxide form was carried out
22 analogously to Template A above.
23

24 Example 3
25 Synthesis of SSZ-25
26

27 0.50 Grams of a 0.55 molar solution of Template B and
28 0.22 gms of isobutyl amine and 0.03 gms of SSZ-25 seeds were
29 mixed with 0.20 gms KOH(s), 0.083 gms of Reheis F-2000
30 hydrated alumina (50-56 wt% aluminum oxide), and 11.4 Ml
31 H₂O. After thorough mixing, 0.90 gms of Cabosil M5 was
32 blended in as silica source. The reaction mixture was
33 heated in the Teflon cup of a Parr 4745 reactor at 170°C at
34 43 rpm for 4 days. Workup produced crystalline SSZ-25.

-40-

Example 4Synthesis of SSZ-25

In this example, the use of a nonquaternized amine is demonstrated. The same experiment was run as in Example 3, except 1 millimole of 1-adamantanamine (Aldrich) replaced the Template B. The product was again SSZ-25.

Example 5Synthesis of SSZ-25

This example also demonstrates the use of a nonquaternized amine. 12.5 Grams of Reheis F-2000 was dissolved in 30 gms of KOH(s) and 1500 Ml H₂O, 7.5 gms of 1-adamantanamine (Aldrich Chemical Co.), and 75 gms of 4-methylpiperidine (Aldrich Chemical Co.). 3 Grams of SSZ-25 seed crystals and 437 gms of Ludox AS-30 were added last. The reaction was run in a 1-gallon autoclave with Hastelloy C liner at 170°C and 75 rpm. After 6 days, the product was crystalline SSZ-25.

Refer to Table 3 for a summary of Examples 3-5.

TABLE 3

<u>Ex. No.</u>	<u>Adamantyl Component</u>	<u>Amine</u>	<u>Product</u>
3	Template B	Isobutyl Amine	SSZ-25
4	1-adamantanamine	Isobutyl Amine	SSZ-25
5	1-adamantanamine	4-methylpiperidine	SSZ-25

-41-

Examples 6-9Synthesis of SSZ-25

In these examples, the effectiveness or necessity of the adamantyl quaternary ammonium ion is demonstrated by comparison of reaction products with and without such a component at only a 0.02 molar ratio to silica. This quantity of adamantyl component is insufficient to fill the micropore volume of the growing SSZ-25 and additional organic is needed, and was subsequently found in the micropore system. Table 4 shows the comparative examples.

TABLE 4

SSZ-25 Syntheses With and Without Adamantyl
Quaternary Ammonium Ion Synthesis Promoters^(a)

<u>Ex. No.</u>	<u>Adamantyl</u> <u>Component</u>	<u>Amine</u> ^(b)	<u>SiO₂/</u> <u>Al₂O₃</u>	<u>KOH/SiO₂</u>	<u>Product</u>
6	B	Piperidine	35	0.20	SSZ-25
7	-	Piperidine	35	0.20	ZSM-5
8	B	Cyclopentylamine	35	0.20	SSZ-25
9	-	Cyclopentylamine	35	0.20	ZSM-5

^(a) Experiments carried out as in Example 3.

^(b) Experiments carried out using amine/SiO₂ ratio of 0.20.

B = Template B (Example 2).

Examples 10-12Synthesis of SSZ-25

In these experiments, the variation of the adamantane compound is demonstrated. The experiments are carried out as in Example 3. Recall that in Example 7, the use of

-42-

01 piperidine alone, even in the presence of SSZ-25 seeds,
02 produced ZSM-5.

03

04 Refer to Table 5 for the variations of the adamantane
05 compound.

06

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TABLE 5

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<u>Ex. No.</u>	<u>Adamantyl Component*</u>	<u>Piperidine/SiO₂</u>	<u>SiO₂/ Al₂O₃</u>	<u>KOH/SiO₂</u>	<u>Product</u>
10	A	0.20	35	0.20	SSZ-25
11	C	0.20	35	0.20	SSZ-25
12	D	0.20	35	0.20	SSZ-25

*At a level of 0.02 relative to SiO₂.

A = Template A (Example 1).

C = Quaternized derivative of 1-aminomethyl-adamantane.

D = 1-adamantanol.

Examples 13-20Synthesis of SSZ-25

In these examples, SSZ-25 was formulated, using SSZ-25 as a seed material in two examples and using no seed in two examples to determine whether seed material was necessary to produce SSZ-25. The final product was SSZ-25 in all cases. In the examples where 4-methylpiperidine was used as the amine component, improvement in growth time was observed at three days for the example utilizing seed material. In the examples where isobutylamine was used as the amine component, the growth time was improved by at least a factor of two for the example utilizing seed material.

-43-

01 In these examples, 1 millimole of 1-adamantanamine was mixed
02 with 15 millimoles of silica as SiO₂ and 3 millimoles of the
03 smaller amine. All of the remaining ratios of reactants and
04 run conditions were as in Example 3. In Examples 13-16, the
05 major amine was 4-methylpiperidine. For Examples 17-20, the
06 major amine was isobutylamine. Reaction conditions were
07 substantially the same as those in Example 3. Results are
08 summarized in Table 6.

TABLE 6

12 Effect of seed on type of zeolite produced and growth time
13 for SSZ-25

15	Ex. No.	Amine Component	Seed Used	Growth Time	Product
16	13	4-methylpiperidine	SSZ-25	3 days	SSZ-25 +
17					amorphous.
18	14	4-methylpiperidine	SSZ-25	6 days	SSZ-25
19	15	4-methylpiperidine	none	3 days	amorphous
20	16	4-methylpiperidine	none	6 days	SSZ-25
21	17	isobutylamine	SSZ-25	3 days	SSZ-25
22	18	isobutylamine	SSZ-25	6 days	SSZ-25
23	19	isobutylamine	none	3 days	SSZ-25 +
24					amorphous
25	20	isobutylamine	none	6 days	SSZ-25

Examples 21-28Synthesis of SSZ-32

29 A basic reaction solution was made by combining
30 0.50 millimoles of N,N'-diisopropylimidazolium hydroxide
31 (Template E), 0.20 gram of solid KOH, 0.083 gram of Reheis
32 F-2000 hydrated aluminum hydroxide, and a total of 11.4 ml
33 of water. To this solution, 0.90 gram of Cabosil M-5 fumed
34

- 44 -

01 silica (98%) was added. Finally, 0.20 gram of isobutyl
02 amine was added. These reactants were all combined in the
03 Teflon cup of a Parr 4745 reactor (23 ml capacity). The
04 reactor was sealed and loaded onto a rotating spit in a Blue
05 M oven and heated at 170°C for 6 days while rotating at
06 43 rpm. After this time period, the reactor was cooled in
07 air, the resulting solid product filtered and washed with
08 water in a funnel, and then air-dried. The resulting powder
09 was analyzed by X-ray diffraction (XRD) and found to be
10 SSZ-32. An elemental analysis showed the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio
11 for this product to be 28.

12

13 This reaction was repeated using each in turn the amines
14 listed in Table 7 below in the quantities also shown in that
15 table. The product of each reaction was SSZ-32.

16

17

TABLE 7

18

19	<u>Example No.</u>	<u>Amine</u>	<u>Amount of Amine</u>
20	22	methylamine	0.5g*
21	23	NH_4OH	0.66g**
22	24	butylamine	0.20g
23	25	t-butylamine	0.25g
24	26	dipropylamine	0.22g
25	27	isopropylamine	0.20g
26	28	cyclopentylamine	0.26g

27 *40% aqueous solution

28 **30% aqueous solution

29

30 These examples demonstrate that SSZ-32 can be prepared using
31 very low levels of the organic templating compound, in this
32 case a mole ratio of Template E/ SiO_2 of only 0.033. In
33 fact, this reaction has been successfully conducted with
34 this ratio as low as 0.02. Without the addition of the

-45-

01 small amine (isobutyl amine) the product, SSZ-32, would not
02 be achieved at this low level of templating compound.

03

04

Example 29-39

05

06 A procedure similar to that described in Examples 21-28 was
07 used to prepare the zeolites listed in the table below
08 except that the organic template was N,N,N-trimethyl-
09 1,1,3,3-tetramethyl butyl ammonium hydroxide (Template E')
10 and the amines were those listed in the table below.

11

12 The reaction mixture contained the following mole ratios:

13

14 Template E'/SiO₂ = 0.02

15 Amine/SiO₂ = 0.20

16

17 Also, the reaction mixture contained 0.6 wt. % SSZ-32 seed
18 crystals.

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01	Ex No.	Amine	Growth Time	Product
02	29*	isobutylamine	9 days	SSZ-32 (plus trace amorphous)
03	30*	cyclopentylamine	9 days	SSZ-32
04	31*	isopropylamine	7 days	SSZ-32
05	32*	n-butylamine	7 days	ZSM-5 (plus minor amount of ferrierite)
06	33*	piperidine	7 days	ZSM-5
07	34*	cyclohexylamine	18 days	ferrierite (plus minor amount of cristobalite)
08	35*	1,1,3,3-tetra-methylbutyl amine	7 days	SSZ-32
09	36**	isobutylamine	6 days	SSZ-32 (plus trace cristobalite)
10	37**	isopropylamine	7 days	SSZ-32 (plus cristobalite)
11	38**	n-butylamine	7 days	cristobalite + ZSM-5 + quartz
12	39**	piperidine	7 days	ZSM-5 (plus amorphous material)

16 * Silica source was Nyacol colloidal silica.

17 ** Silica source was Cabosil fumed silica.

19 Example 40

20 Synthesis of SSZ-28

22 The same reaction as described in Example 21 for SSZ-32 was
23 carried out, but with the following changes. The organic
24 templating compound was N,N-dimethyl-3-azonium bicyclo
25 [3.2.2] nonane hydroxide (Template F), and the ratio of
26 Template F/SiO₂ was 0.05 (i.e., 0.75 millimoles of
27 Template F was used in the reaction). The resulting product
28 was found to be SSZ-28 by XRD.

30 This example also demonstrates that zeolites can be prepared
31 by the method of this invention using very low amounts of
32 organic templating compound.

- 47 -

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Example 41

Synthesis of EU-1

The same reaction using the same molar quantities described in Example 40 was carried out with the exception that the organic templating compound was the diguaternary ammonium compound 1,6-N,N,N,N',N',N'-hexamethyl hexamethylene diammonium hydroxide (Template G). The resulting product was analyzed by XRD and found to be zeolite EU-1.

Example 42

Synthesis of EU-1

0.62 Gram of a solution of 4-benzyl-N,N-dimethylpiperidinium hydroxide (0.485 mmol OH/g), 0.08 gram of Reheis F2000 hydrated aluminum hydroxide, and 0.20 gram of solid KOH were dissolved in 11.4 grams of water. Isobutyl amine (0.22 gram) was added to this solution, followed by the addition of 0.90 gram of Cabosil M-5 fumed silica. The resulting reaction mixture was mixed thoroughly and sealed in a Parr 4745 reactor which was then heated to 170°C and rotated at 43 rpm. After 16 days the reaction was complete, and the product which was isolated was determined by XRD to be EU-1.

Example 43

Synthesis of SSZ-35

The same reaction using the same molar quantities described in Example 40 was carried out, except that the organic templating compound used was the polycyclic compound having formula VI above (Template H). The resulting product was determined by XRD to be SSZ-35.

- 48 -

Example 44Synthesis of ZSM-22 type structures

The same reaction described in Example 21 was carried out, except that the organic templating compound was 2,6-dimethylpiperidine (Template I) which was used in the ratio of Template I/SiO₂ of 0.02. The resulting product was determined by XRD to be ZSM-22 type structures.

Example 45

Using the procedure of Example 21 and the amines and organic templating compounds shown in Table 8, the zeolites also shown in Table 8 were prepared.

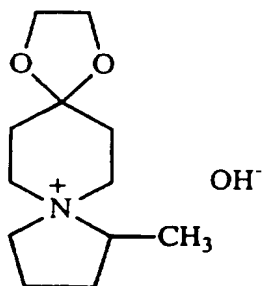
TABLE 8

<u>Zeolite</u>	<u>Amine</u>	<u>Amount of Amine</u>	<u>Template</u>
SSZ-28	cyclopentylamine	0.26g	F
SSZ-25	piperidine	0.26g	F
EU-1	cyclopentylamine	0.26g	G
SSZ-35	cyclopentylamine	0.26g	H
SSZ-35	piperidine	0.26g	H
ZSM-22	cyclopentylamine	0.26g	I
ZSM-22	piperidine	0.26g	I

Example 46Synthesis of ZSM-12

The same procedure described in Example 21 was performed, except that a piperidine-based templating agent (Template J) having the following structure:

- 49 -



was used in place of the imidazolium-based template employed in Example 21. After 23 days of heating at 170°C, the product was isolated and identified as ZSM-12. Elemental analysis showed the product to have a SiO₂/Al₂O₃ mole ratio of 30.

- 50 -

01 WHAT IS CLAIMED IS:

02

03 1. A method for preparing a zeolite selected from the
04 group consisting of large pore zeolites, medium pore
05 zeolites having unidimensional channels, and small pore
06 zeolites, said method comprising:

07

08 A. forming an aqueous reaction mixture comprising
09 (1) a source of an oxide selected from silicon
10 oxide, germanium oxide and mixtures thereof; (2) a
11 source of an oxide selected from aluminum oxide,
12 gallium oxide, iron oxide, boron oxide, titanium
13 oxide and mixtures thereof; (3) a source of an
14 alkali metal oxide; (4) an amine component
15 comprising at least one amine containing one to
16 eight carbon atoms, ammonium hydroxide, and
17 mixtures thereof, and (5) an organic templating
18 compound capable of forming said zeolite in the
19 presence of said amine, wherein said amine is
20 smaller than said organic templating compound; and

21

22 B. maintaining said aqueous mixture under sufficient
23 crystallization conditions until crystals are
24 formed.

25

26 2. The method of Claim 1 wherein the large pore zeolite
27 has unidimensional channels.

28

29 3. The method of Claim 1 wherein the large pore zeolite
30 has multidimensional channels.

31

32 4. The method of Claim 1 wherein said organic templating
33 compound is selected from the group consisting of

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-51-

01 quaternary ammonium ions, cyclic amines and polar
02 adamantyl derivatives.

03

04 5. The method of Claim 1 wherein the amine component
05 comprises an aliphatic, cycloaliphatic or heterocyclic
06 amine, ammonium hydroxide or mixtures thereof.

07

08 6. The method of Claim 5 wherein the amine component
09 comprises a compound selected from the group consisting
10 of isobutylamine, methylamine, ammonium hydroxide,
11 butylamine, t-butylamine, dipropylamine,
12 isopropylamine, cyclopentylamine, piperidine,
13 4-methylpiperidine, cyclohexylamine, and
14 1,1,3,3-tetramethylbutyl amine.

15

16 7. The method of Claim 1 wherein said aqueous mixture
17 further comprises a sufficient amount of seed material.

18

19 8. The method of Claim 1 wherein the reaction mixture
20 comprises the following in terms of mole ratios:

21

22	M/YO ₂	0.01-0.50
23	OH ⁻ /YO ₂	0.01-0.60
24	H ₂ O/YO ₂	10-120
25	Q/YO ₂	0.02-1.00
26	YO ₂ /W ₂ O ₃	10-200
27	Z/YO ₂	0.05-1.00

28

29 where M is an alkali metal, Y is silicon, germanium, or
30 both; Q is the organic templating compound, Z is the
31 amine component; and W is aluminum, gallium, iron,
32 boron, titanium or mixtures thereof.

33

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-52-

- 01 9. The method of Claim 8 wherein the reaction mixture
02 comprises the following in terms of mole ratios:
03
04 M/YO₂ 0.10-0.20
05 OH⁻/YO₂ 0.10-0.30
06 H₂O/YO₂ 20-50
07 Q/YO₂ 0.02-0.10
08 YO₂/W₂O₃ 15-120
09 Z/YO₂ 0.20-0.40
10
- 11 10. The method of Claim 4 wherein the zeolite has, after
12 calcination, the X-ray diffraction pattern of Table 2.
13
- 14 11. The method of Claim 10 wherein the organic templating
15 compound comprises adamantanamine.
16
- 17 12. The method of Claim 11 wherein said adamantanamine
18 comprises at least one adamantanamine from the group ,
19 1-adamantanamine or 2-adamantanamine.
20
- 21 13. The method of Claim 11 wherein the amine component
22 comprises isobutylamine, 4-methylpiperidine,
23 cyclopentylamine, or piperidine.
24
- 25 14. The method of Claim 11 wherein the organic templating
26 compound comprises adamantanol.
27
- 28 15. The method of Claim 14 wherein said adamantanol
29 comprises at least one adamantanol from the group
30 1-adamantanol and 2-adamantanol.
31
- 32 16. The method of Claim 14 wherein the amine component
33 comprises piperidine or isobutylamine.
34

- 53 -

- 01 17. The method of Claim 4 wherein the as-synthesized
02 zeolite has the X-ray diffraction pattern of Table A.
03
- 04 18. The method of Claim 17 wherein the organic templating
05 compound comprises an N,N'-disubstituted imidazolium
06 compound or N,N,N-trialkyl-1,1,3,3-tetraalkyl butyl
07 ammonium cation.
08
- 09 19. The method of Claim 18 wherein the imidazolium compound
10 is an N,N'-diisopropylimidazolium cation, or
11 N-methyl-N'-isopropylimidazolium cation.
12
- 13 20. The method of Claim 18 wherein the N,N,N-trialkyl-
14 1,1,3,3-tetraalkyl butyl ammonium cation is a N,N,N-
15 trimethyl-1,1,3,3-tetramethylbutyl ammonium cation.
16
- 17 21. The method of Claim 18 wherein the organic templating
18 compound comprises an N,N'-disubstituted imidazolium
19 compound and the amine component comprises a compound
20 selected from the group consisting of isobutylamine,
21 methylamine, ammonium hydroxide, butylamine,
22 t-butylamine, dipropylamine, isopropylamine, and
23 cyclopentylamine.
24
- 25 22. The method of Claim 18 wherein the organic templating
26 compound comprises an N,N,N-trialkyl-1,1,3,3-tetraalkyl
27 butyl ammonium cation and the amine component is
28 selected from the group consisting of isobutylamine,
29 cyclopentylamine, isopropylamine and 1,1,3,3-
30 tetramethylbutyl amine.
31
- 32 23. The method of Claim 4 wherein the zeolite has, in the
33 as-synthesized form, the X-ray diffraction pattern of
34 Table B.

- 54 -

01 24. The method of Claim 23 wherein the organic templating
02 compound comprises a piperidine derivative.

03

04 25. The method of Claim 24 wherein the piperidine
05 derivative is 2,6-dimethylpiperidine.

06

07 26. The method of Claim 24 wherein the amine component
08 comprises isobutylamine, cyclopentylamine or
09 piperidine.

10

11 27. The method of Claim 23 wherein the organic templating
12 compound comprises imidazole salts of the formula

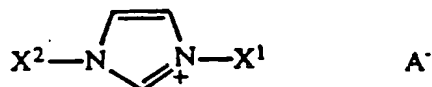
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21 wherein X¹ and X² independently represent a linear alkyl
22 group containing from 1 to about 10 carbon atoms,
23 and A^o represents an anion which is not detrimental to
24 the formation of the zeolite.

25

26 28. The method of Claim 4 wherein the zeolite has, in the
27 as-synthesized form, the X-ray diffraction pattern of
28 Table C.

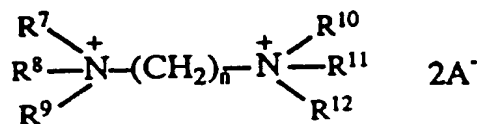
29

30 29. The method of Claim 28 wherein the organic templating
31 compound is selected from the group consisting of
32 N,N-dimethyltropinium and N,N-dimethyl-3-azonium
33 bicyclo[3.2.2]nonane cations.

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-55-

- 01 30. The method of Claim 29 wherein the amine component
 02 comprises isobutylamine, cyclopentylamine, or
 03 piperidine.
 04
- 05 31. The method of Claim 4 wherein the zeolite has, in the
 06 as-synthesized form, the X-ray diffraction pattern of
 07 Table D.
 08
- 09 32. The method of Claim 31 wherein the organic templating
 10 compound comprises alkylated derivatives of a
 11 polymethylene diamine having the formula
 12



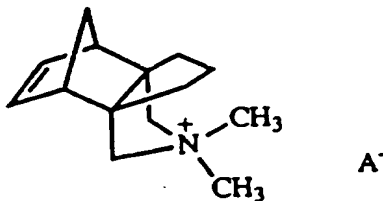
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 19 wherein n is in the range from 3 to 12, R⁷ to R¹², which
 20 may be the same or different, are hydrogen, alkyl or
 21 hydroxyalkyl groups, containing from 1 to 8 carbon
 22 atoms and up to five of the groups R⁷-R¹² can be
 23 hydrogen, and A⁻ is an anion which is not detrimental
 24 to the formation of the zeolite.
 25

- 26 33. The method of Claim 32 wherein the organic templating
 27 compound comprises a 1,6-N,N,N,N',N',N'-hexamethyl
 28 hexamethylene diammonium cation.
 29
- 30 34. The method of Claim 32 wherein the amine component
 31 comprises isobutylamine or cyclopentylamine.
 32
 33
 34

-56-

- 01 35. The method of Claim 31 wherein the organic templating
02 compound is a 4-benzyl-N,N-dimethylpiperidinium
03 compound.
04
- 05 36. The method of Claim 35 wherein the amine component
06 comprises isobutylamine.
07
- 08 37. The method of Claim 4 wherein the zeolite has, in the
09 as-synthesized form, the X-ray diffraction pattern of
10 Table E.
11

- 12 38. The method of Claim 37 wherein the organic templating
13 compound is selected from the group consisting of an
14 N-ethyl-N-methyl-9-azoniabicyclo[3.3.1]nonane cation
15 and a compound having the following formula:
16

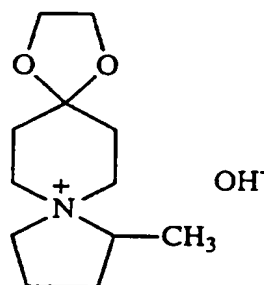


- 21 where A⁻ is an anion which is not detrimental to the
22 formation of the zeolite.
23

- 24 39. The method of Claim 38 wherein the amine component
25 comprises isobutylamine, cyclopentylamine or
26 piperidine.
27
- 28 40. The method of Claim 4 wherein the zeolite is
29 ferrierite.
30
- 31 41. The method of Claim 40 wherein the organic templating
32 compound comprises an N,N,N-trialkyl-1,1,3,3-tetraalkyl
33 butyl ammonium cation.
34

-57-

- 01 42. The method of Claim 41 wherein the N,N,N-trialkyl-
02 1,1,3,3-tetraalkyl butyl ammonium cation is N,N,N-
03 triethyl-1,1,3,3-tetramethylbutyl ammonium cation.
04
- 05 43. The method of Claim 41 wherein the amine component
06 comprises cyclohexylamine.
07
- 08 44. The method of Claim 4 wherein the as-synthesized
09 zeolite has the X-ray diffraction pattern of Table F.
10
- 11 45. The method of Claim 44 wherein the organic templating
12 compound comprises a compound having the following
13 formula:
14



- 21 46. The method of Claim 45 wherein the amine component
22 comprises isobutylamine.
23
- 24 47. A zeolite selected from the group consisting of large
25 pore zeolites, medium pore zeolites having
26 unidimensional channels, and small pore zeolites having
27 an as-synthesized molar composition in an anhydrous
28 state of $(0.02 \text{ to } 2.0)Q:(0.02 \text{ to } 1.0)Z:(0.1 \text{ to } 2.0)M_2O:W_2O_3:(10 \text{ to } 200)YO_2$, wherein M is an alkali metal
29 cation; W is selected from aluminum, gallium, iron,
30 boron, titanium and mixtures thereof; Y is selected
31 from silicon, germanium, and mixtures thereof; Z is an
32 amine component comprising at least one amine
33 containing from one to eight carbon atoms, ammonium
34

- 58 -

- 01 hydroxide, and mixtures thereof, Q is an organic
02 templating compound capable of forming the zeolite in
03 the presence of said amine component, wherein said
04 amine is smaller than the organic templating compound.
05
- 06 48. The zeolite of Claim 47 having, after calcination, the
07 X-ray diffraction pattern of Table 2.
08
- 09 49. The zeolite of Claim 47 having, in the as-synthesized
10 form, the X-ray diffraction pattern of Table A.
11
- 12 50. The zeolite of Claim 47 having, in the as-synthesized
13 form, the X-ray diffraction pattern of Table B.
14
- 15 51. The zeolite of Claim 47 having, in the as-synthesized
16 form, the X-ray diffraction pattern of Table C.
17
- 18 52. The zeolite of Claim 47 having, in the as-synthesized
19 form, the X-ray diffraction pattern of Table D.
20
- 21 53. The zeolite of Claim 47 having, in the as-synthesized
22 form, the X-ray diffraction pattern of Table E.
23
- 24 54. The zeolite of Claim 47 having, in the as-synthesized
25 form, the X-ray diffraction pattern of Table F.
26
27
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34

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/05984

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 39/02, 39/42, 39/44, 39/48

US CL : 423/703, 704, 705, 706, 707, 708; 502/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/703, 704, 705, 706, 707, 708; 502/62

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US, A, 5,350,722 (Joly et al.) 27 September 1994, col's 8 and 9 lines 45-11.	1, 2, 4-6, 8, 9, 44, 47 and 54 -- 7
X	US, A, 4,857,288 (Marcus et al.) 15 August 1989, col's 8 - 10.	1, 4, 8, 9 and 47
X	GB, A, 2,193,202 (Stewart) 03 February 1988, Table 1 p. 2, p. 4 lines 49-51 and page 16.	1, 3-6, 8, 9, 28, 47 and 51
Y	US, A, 4,205,053 (Rollmann et al.) 27 May 1980, col. 12 lines 42-58.	1-54

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* "A" document defining the general state of the art which is not considered to be of particular relevance	* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* "E" earlier document published on or after the international filing date	* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* "A" document member of the same patent family
* "O" document referring to an oral disclosure, use, exhibition or other means	
* "P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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